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PATENT ABSTRACTS OF JAPAN

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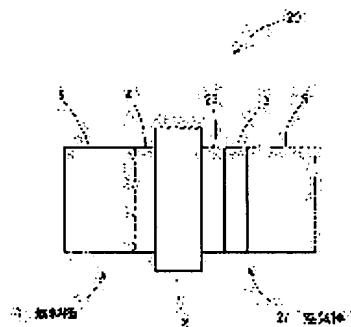
(21)Application number : 2003-142858 (71)Applicant : EQUOS RESEARCH CO LTD
(22)Date of filing : 21.05.2003 (72)Inventor : YAMAMOTO TAIZO

(54) ELECTRODE FOR FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new method for preventing a polymer electrolyte material from being decomposed by a radical resulting from hydrogen gas, which has passed through an electrolytic film, in an air electrode side catalyst layer of a fuel cell.

SOLUTION: The air electrode side catalyst layer has a first catalyst layer on a side of the electrolytic film and a second catalyst layer on a side of a diffusion layer, where a gas transfer resistance of the first catalyst layer is higher than a gas transfer resistance of the second catalyst layer.



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CLAIMS

[Claim(s)]

[Claim 1]

It is the electrode used for a fuel cell, and the air pole side comes to carry out the laminating of a catalyst bed and the diffusion layer to an electrolyte membrane, It is the electrode for fuel cells with which said catalyst bed is equipped with the 1st catalyst bed by the side of said electrolyte membrane, and the 2nd catalyst bed by the side of said diffusion layer, and said 1st catalyst bed is characterized by the thing with strong gas migration resistance rather than said 2nd catalyst bed.

[Claim 2]

The pore size of said 1st catalyst bed is an electrode [smaller than the porosity of said 2nd catalyst bed] for fuel cells according to claim 1 characterized by things.

[Claim 3]

The void content of said 1st catalyst bed is an electrode [smaller than the void content of said 2nd catalyst bed] for fuel cells according to claim 1 characterized by things.

[Claim 4]

The fuel cell equipped with the electrode for fuel cells according to claim 1 to 3.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]

This invention relates to amelioration of the electrode for fuel cells.

[0002]

[Description of the Prior Art]

A fuel cell is a fuel electrode (it is also called a hydrogen pole when using hydrogen as a fuel electrode), and an air pole (since oxygen is reactant gas, it is also called an oxygen pole.). Moreover, while also calling it an oxidation pole, it is the configuration that the solid polymer electrolyte film was *** (ed).

An electron is generated with progress of electrochemical reaction and the electromotive force of such a fuel cell of a configuration is generated by taking out this electron to an external circuit, as a result of supplying fuel gas to a fuel electrode side (anode) and supplying oxidation gas to an air pole side. That is, the hydrogen ion obtained with a fuel electrode (anode) can take out the electrical energy by a series of electrochemical reaction which the electron which moved the inside of the electrolyte membrane containing moisture to the air pole (cathode) side, and was obtained with the fuel electrode (anode) moves to an air pole (cathode) side through an external load, reacts with the oxygen in oxidation gas (air is included), and refines water with the gestalt of a proton (H_3O^+).

[0003]

In such a fuel cell, an air pole is the configuration which carried out the laminating of a catalyst bed and the diffusion layer one by one from the electrolyte membrane side. In order to obtain a high output with a fuel cell, this catalyst bed used the carbon black from which structure developed for catalyst support, the void content was gathered, and set the chief aim to enlarge pore size, and was constituted. Since oxygen required for a reaction is contained only about 20% in air, this is because high gaseous diffusion nature is called for by the catalyst bed, in order to obtain the high engine performance. That is, the air of an amount comes to be enough supplied to the whole region of a catalyst bed by making gas migration resistance in a catalyst bed as small as possible.

[0004]

[Problem(s) to be Solved by the Invention]

However, the high gaseous diffusion nature in this catalyst bed has the next technical problem.

The hydrogen by which the fuel cell is supplied to the fuel electrode side in the open circuit (OCV) condition or the low-load-driving condition is not altogether used by generation of electrical energy, but penetrates an electrolyte membrane gradually, and reaches an air pole side (this phenomenon becomes remarkable especially, when an electrolyte membrane is thin). If metal ions, such as Fe^{++} , are contained as contamination also in the minute amount, this will serve as a catalyst, and a part of hydrogen which reached the air pole side will react with oxygen, and it will generate a hydrogen peroxide. This hydrogen peroxide generates a hydroxy radical (-OH) under an acid ambient atmosphere. Since this radical has powerful oxidizing power, it has a possibility of carrying out oxidative degradation also of the electrolyte polymeric materials contained in a catalyst bed.

therefore, in the former, electrolyte polymeric materials are disassembled by catching the metal ion used as the catalyst of hydrogen-peroxide generating by the chelating agent, and blending an antioxidant -- thing prevention is carried out (one to patent reference 5 reference).

[0005]

[Patent reference 1]

JP,2003-86187,A

[Patent reference 2]

JP,2003-20308,A

[Patent reference 3]

JP,2002-343132,A

[Patent reference 4]

JP,2001-223015,A

[Patent reference 5]

JP,2001-118591,A

[0006]

[Problem(s) to be Solved by the Invention]

Disassembly of the polymeric materials of an electrolyte membrane will be controlled by adding a chelating agent and an antioxidant.

However, adding the drugs applied in a fuel cell system not only leads to a cost rise, but the stability of the drugs itself is not checked.

Then, this invention aims at offer of the new policy which prevents disassembly of the electrolyte polymeric materials by the hydrogen peroxide.

[0007]

[Means for Solving the Problem]

When this invention person took lessons from decomposition prevention of the electrolyte polymeric materials by the hydrogen peroxide and came examination in piles wholeheartedly, he hit on an idea of "generating a radical chiefly in a catalyst bed in a diffusion layer side (part which is separated from an electrolyte membrane)" to a header and this invention.

That is, it is the electrode used for a fuel cell, and the air pole side comes to carry out the laminating of a catalyst bed and the diffusion layer to an electrolyte membrane,

It is the electrode for fuel cells with which said catalyst bed is equipped with the 1st catalyst bed by the side of said electrolyte membrane, and the 2nd catalyst bed by the side of said diffusion layer, and said 1st catalyst bed is characterized by the thing with high gas migration resistance rather than said 2nd catalyst bed.

[0008]

Thus, while migration of the hydrogen which has penetrated the electrolyte membrane is barred by the 1st catalyst bed according to the constituted electrode for fuel cells, it oxidizes in the 1st catalyst bed concerned, and the amount which reaches the 2nd catalyst bed by the side of a diffusion layer decreases. Since it has become clear that it is easier to generate in the diffusion layer side of the air pole side catalyst beds, a radical can control generating of the radical as the whole air pole side catalyst bed according to the above-mentioned structure.

[0009]

[Embodiment of the Invention]

This invention is based on the following property in the air pole side catalyst bed which this invention person found out like previous statement.

Generate a radical chiefly in a catalyst bed in a diffusion layer side (part which is separated from an electrolyte membrane).

[0010]

This knowledge was acquired by the experiment explained below.

First, the fuel cell 1 of the example of a comparison shown in drawing 1 was produced. This fuel cell 1 sandwiches the solid-state polyelectrolyte film 2 which consists of Nafion (Nafion112 made from Du Pont: brand name) by the air pole side catalyst bed 3 and the fuel electrode side catalyst bed 4, and the diffusion layer 5 is further formed in the outside of each catalyst beds 3 and 4. In addition, this fuel cell 1 is enclosed by casing which is not illustrated, and the hole for ***** (ing) air to an air pole 7 and the hole for ***** (ing) hydrogen gas to a fuel electrode 8 are prepared in this casing.

[0011]

The air pole side catalyst bed 3 and the diffusion layer 5 were formed as follows.

First, a diffusion layer 5 is formed. The slurry which mixed PTFE dispersion (for example, Pori Flon D-1 (trade name) by Daikin Industries, LTD.) with water-repellent carbon black (for example, DENKI KAGAKU KOGYO DIN a turnip rack (trade name)) is applied to both sides of a carbon cross (for example, GF[by Nippon Carbon Co., Ltd.]-20- P7 (trade name)), and it calcinates at 360 degrees C among a nitrogen air current. At this time, it is appropriate that consider the PTFE content of a spreading layer and coverage

considers as one side 2 - 10 mg/cm² 20 to 50%.

[0012]

Then, Pt support carbon powder catalyst of Pt40 - 60wt% content and an electrolytic solution (5%Nafion (brand name) solution made from Aldrich) are mixed, it applies and dries on a diffusion layer with a spray method or screen printing, and the air pole side catalyst bed 3 is obtained. As for the amount of catalyst support, it is desirable to consider per [0.2] catalyst bed area - as 0.6 mg/cm².

An air pole 7 consists of an air pole side catalyst bed 3 and a diffusion layer 5.

[0013]

On the other hand, the fuel electrode side catalyst bed 4 was formed as follows. Pt support carbon powder catalyst of Pt20 - 40wt% content and an electrolytic solution (5%Nafion (brand name) solution made from Aldrich) are mixed, it applies and dries on a diffusion layer with a spray method or screen printing, and the fuel electrode side catalyst bed 4 is obtained. As for the amount of catalyst support, it is desirable to consider per [0.1] catalyst bed area - as 0.3 mg/cm².

A fuel electrode 8 consists of a fuel electrode side catalyst bed 4 and a diffusion layer 5.

[0014]

The solid-state polyelectrolyte film 2 is inserted between the air poles 7 and fuel electrodes 8 which were obtained as mentioned above, and it joins by hot pressing. the conditions of a hotpress -- temperature: -- it is desirable to consider as 120-160 degrees C, pressure:30-100 kg/cm², and press time:1 - 5 minutes.

[0015]

Thus, after fully performing energization processing in advance to the fuel cell 1 of obtained drawing 1 and being activated to it, set cel temperature as 80 degrees C, two poles 7 and 8 are made to fully dry dry N2 gas as ******, and the condition of a fuel cell 1 is initialized. This is for the difference in the damp or wet condition in early stages of an electrolyte membrane 2 protecting changing the amount of transparency of the hydrogen of an electrolyte membrane. Then, a part (SUTOIKI ratio 4 at 0.05 A/cm²) for 0.03L/is supplied for heavy hydrogen (80 degrees C, saturation humidification) to a fuel electrode 8 side, a part (SUTOIKI ratio 17 at 0.05 A/cm²) for 0.32L/is sent for air (humidifying [a room temperature / no]), and a fuel cell 1 is operated by the open circuit condition. The end of a glass capillary is contacted to an air pole 7, and the other end of a capillary is connected to a high vacuum exhauster and a mass spectrometer. About seven air pole [which was sampled through the capillary] gas constituents are identified by in-situ with a mass spectrometer.

[0016]

The result of identification is shown in drawing 2 . In drawing 2 , 10 minutes of the beginning showed the initialization phase and supplied heavy hydrogen (D2) gas to the fuel electrode 8 side after [of measurement initiation] 10 minutes. Consequently, the concentration of peroxidation heavy hydrogen (D2O2) and heavy hydrogen fluoride (DF) is increasing. The heavy hydrogen which passed the electrolyte membrane 2 oxidizes in the air pole side catalyst bed 3, and turns into peroxidation heavy hydrogen, this peroxidation heavy hydrogen produces a radical (-DH) under an acid ambient atmosphere, and this is considered that this disassembled the electrolyte polymeric materials of a catalyst bed 3, and generated heavy hydrogen fluoride.

[0017]

Next, in the fuel cell of drawing 1 , the monitor of the amount of generation of the hydrogen fluoride (HF) when changing the pore structure of the air pole side catalyst bed 3 was carried out. A result is shown in drawing 3 . The line of the bottom in drawing shows HF concentration. Drawing 3 shows that the concentration of HF becomes high as a void content becomes large. That is, the yield of a hydroxy radical increases as a catalyst bed 3 becomes a non-dense and the gas migration resistance becomes low.

By the catalyst bed with low gas migration resistance, this is considered to become easy to generate the hydrogen peroxide which is a source of radical formation, in order that the hydrogen which has passed the electrolyte membrane 2 may spread round the whole catalyst bed easily.

the result of drawing 3 -- "catalyst bed -- a non-dense (gas migration resistance smallness), so that -- the yield of a hydrogen peroxide -- increasing -- an another side catalyst bed -- nectar (gas migration resistance size), so that -- the yield decreases -- " -- it can check.

In addition, the Measuring condition of drawing 3 is as a publication among drawing. Each output voltage in each sample is a little less than [1V].

[0018]

In the fuel cell 1 of drawing 1 , although Pt support carbon catalyst was used as an air pole side catalyst bed 4, the condition of hydrogen fluoride generating by the open circuit condition about what made this Pt-Black

(other manufacture conditions are the same) is shown in drawing 4 . The roughness factor of what has Pt support carbon catalyst in a catalyst bed 4, and the thing which has a Pt-Black catalyst was unified, and both gas migration resistance was substantially made equal.

The result of drawing 4 shows that the yield of hydrogen fluoride is decreasing notably, when a Pt-Black catalyst is adopted. In order that the oxygen molecule which adsorbed on platinum may dissociate this easily, it is considered to react with the hydrogen which has penetrated the electrolyte membrane 2, and for water to only generate, and to be hard to generate the hydrogen peroxide which is a source of radical formation.

[0019]

Like previous statement, compared with Pt support carbon catalyst, with the Pt-Black catalyst, as it was shown in drawing 5 on the assumption that the yield of hydrogen fluoride becomes small, the air pole side catalyst bed was used as the layer which consists either of a Pt support carbon catalyst as two-layer structure (the 1st catalyst bed 13a, the 2nd catalyst bed 13b), and another side was used as the layer which consists of a Pt-Black catalyst. In addition, in drawing 5 , the same sign is given to the same element as drawing 1 , and the explanation is omitted. The result of monitor Perilla frutescens (L.) Britton var. crispa (Thunb.) Decne. is shown for the amount of hydrogen fluoride generation when carrying out open circuit actuation of the fuel cell 10 which has such an air pole side catalyst bed in drawing 6 .

The result of drawing 6 shows that the amount of generation of hydrogen fluoride is falling notably, when the Pt-Black catalyst bed has been arranged to the diffusion layer 5 side. If an example is taken by a Pt-Black catalyst bed having small generating of HF, it will be presumed that the generating part of a radical is located in a diffusion layer side in a catalyst bed.

It can check this new knowledge by this invention person, and "generate a radical chiefly in a catalyst bed in a diffusion layer side (part which is separated from an electrolyte membrane)" from the result of drawing 4 and drawing 6 .

In addition, the Measuring condition of drawing 6 is as a publication among drawing. Each output voltage in each sample is a little less than [1V].

[0020]

The fuel cell 20 of an example is shown in drawing 7 . In drawing 7 , the same sign is given to the same element as drawing 1 , and the explanation is omitted.

In the fuel cell 20 of an example, the air pole side catalyst bed (the 2nd catalyst bed) 3 is formed in a diffusion layer 5 like the case of drawing 1 (thickness: about 10 micrometers). Then, a void content and/or pore size select small that to which gas migration resistance becomes large in advance from the 2nd catalyst bed 3 by measuring pore distribution of the fine particles which mixed Pt support carbon powder catalyst and the electrolyte, and were dried. This catalyst and electrolytic solution are mixed, this is applied and dried on the 2nd catalyst bed 3 with a spray method, screen printing, etc., the 1st catalyst bed 23 is formed (thickness: about 2-5 micrometers), and it considers as the air pole 27 of an example. That organization of this 1st catalyst bed 23 is more precise than the 2nd catalyst bed 3, and its gas migration resistance is high. In the example, the amount of catalyst support in this 1st catalyst bed 23 was made per [0.01] area of a catalyst bed - into 0.2 mg/cm².

[0021]

Thus, the result of monitor Perilla frutescens (L.) Britton var. crispa (Thunb.) Decne. is shown for the hydrogen fluoride yield when carrying out open circuit actuation of the fuel cell 20 of the acquired example in drawing 8 . The example of a comparison shows the fluorine yield of the fuel cell 1 of drawing 1 . In addition, the Measuring condition of drawing 8 is as a publication all over drawing. Each output voltage in each sample is a little less than [1V].

according to the fuel cell 20 of the result of drawing 8 to an example -- the time of the balance 10 hours (600 minutes) after test initiation -- also setting -- the yield of hydrogen fluoride -- about [of the example of a comparison] -- it turns out that it is decreasing to one half. The absolute magnitude of hydrogen which reaches to the 2nd catalyst bed which has the potential which is easy to generate a radical since migration of the hydrogen which has penetrated the electrolyte membrane 2 is barred by the 1st catalyst bed of a dense configuration becomes small, and this is considered because the yield of the hydrogen peroxide which has and serves as a radical source of release became small as the whole catalyst bed.

[0022]

If the 1st high layer of gas migration resistance is prepared in an air pole side catalyst bed, it will be apprehensive about the diffusibility of air falling and the output characteristics of a fuel cell declining. However, as shown in drawing 9 , the fuel cell (drawing 7) of an example showed the equivalent volt

ampere characteristic as substantially as the fuel cell (drawing 1) of the example of a comparison. That is, according to the fuel cell 20 of an example, generation of a radical can be controlled where an operating characteristic is maintained. Therefore, disassembly of electrolyte polymeric materials will be controlled and the stable generation-of-electrical-energy capacity will be maintained.

[0023]

This can be made into a three-tiered structure thru/or the multilayer structure beyond it although the air pole side catalyst bed is made into two-layer structure in the example of drawing 7 . In this case, it is desirable to turn gas migration resistance of each class to a diffusion layer, and to make it small one by one from an electrolyte membrane side. Furthermore, in an air pole side catalyst bed, the gas migration resistance can also be dwindled towards a diffusion layer from an electrolyte membrane side.

[0024]

In the air pole side catalyst bed, it was checked by this invention person that more radicals occur in the part by the side of a diffusion layer. Therefore, property lowering of an air pole side catalyst bed can be effectively aimed at by giving a radical generating prevention means intensively to the part concerned. As the radical generating prevention means concerned, the activity of the chelating agent and antioxidant which are proposed by the patent reference 1-5 besides the activity (refer to drawing 3) of a compact layer and the activity (refer to drawing 4) of a Pt-Black catalyst can be considered.

[0025]

[Effect of the Invention]

As explained above, according to invention of claim 1, it had the 1st catalyst bed by the side of an electrolyte membrane, and the 2nd catalyst bed by the side of a diffusion layer as an air pole side catalyst bed, and gas migration resistance of the 1st catalyst bed was made higher than the 2nd catalyst bed. While migration of the hydrogen which has penetrated the electrolyte membrane is barred by the 1st catalyst bed by this, it oxidizes in the 1st catalyst bed concerned, and the amount which reaches the 2nd catalyst bed by the side of a diffusion layer decreases. Since it has become clear that it is easier to generate in the diffusion layer side of the air pole side catalyst beds, a radical can control generating of the radical as the whole air pole side catalyst bed according to the above-mentioned structure. Therefore, disassembly of the electrolyte polymeric materials in an air pole side catalyst bed is controlled, and stable maintenance of the engine performance is carried out.

According to invention of claim 2, in order to raise the gas migration resistance in claim 1, the pore size of the 1st catalyst bed was made smaller than the pore size of the 2nd catalyst bed. Generating of the radical as the whole air pole side catalyst bed can be controlled according to this structure.

According to invention of claim 3, in order to raise the gas migration resistance in claim 1, the void content of the 1st catalyst bed is smaller than the void content of the 2nd catalyst bed. Generating of the radical as the whole air pole side catalyst bed can be controlled according to this structure.

According to invention of claim 4 which furthermore applied these electrodes for fuel cells to the fuel cell, the life of a fuel cell will improve.

[0026]

This invention is not limited to explanation of the gestalt of implementation of the above-mentioned invention, and an example at all. It does not deviate from the publication of a claim but deformation modes various in the range this contractor can hit on an idea of easily are also contained in this invention.

[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is the mimetic diagram showing the configuration of the fuel cell of the example of a comparison of this invention.

[Drawing 2] Drawing 2 is a chart which shows generating of D2O2 and DF of the fuel cell of the example of a comparison.

[Drawing 3] Drawing 3 is a chart which shows the magnitude of gas migration resistance and the relation of generating (namely, generating of a radical) of HF to an air pole side catalyst bed.

[Drawing 4] Drawing 4 is a chart which shows the relation of generating (namely, generating of a radical) between Pt support carbon catalyst, a Pt-Black catalyst, and HF in an air pole side catalyst bed.

[Drawing 5] Drawing 5 is the mimetic diagram showing the configuration of the fuel cell of the example of an experiment.

[Drawing 6] Drawing 6 is a chart which shows the relation of generating (namely, generating of a radical) of HF in the fuel cell of drawing 5 .

[Drawing 7] Drawing 7 is the mimetic diagram showing the configuration of the fuel cell of an example.

[Drawing 8] Drawing 8 is a chart which shows the relation of generating (namely, generating of a radical) of

HF of the fuel cell of an example and the example of a comparison.

[Drawing 9] Drawing 9 is a chart which shows the operating characteristic (current potential property) of the fuel cell of an example and the example of a comparison.

[Brief Description of Notations]

1, 10, 20 Fuel cell

2 Electrolyte Membrane

3 Air Pole Side Catalyst Bed

4 Fuel Electrode Side Catalyst Bed

5 Diffusion Layer

7 Air Pole

8 Fuel Electrode

13a, 23 The 1st catalyst bed

13b, 3 The 2nd catalyst bed

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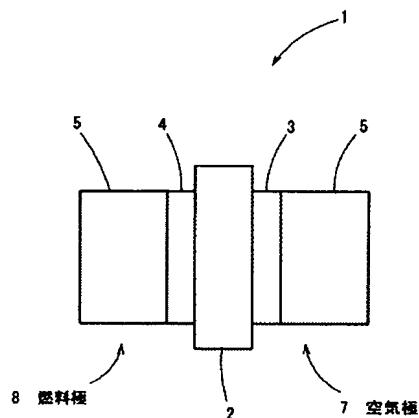
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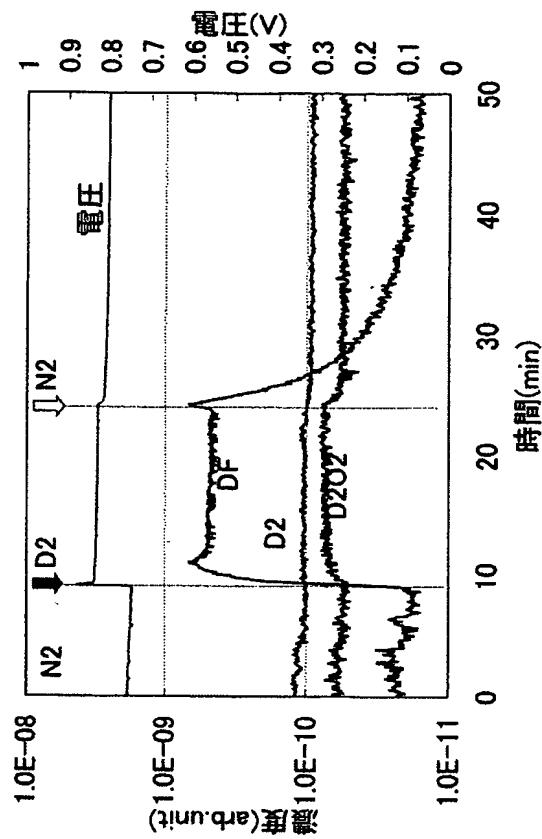
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DRAWINGS

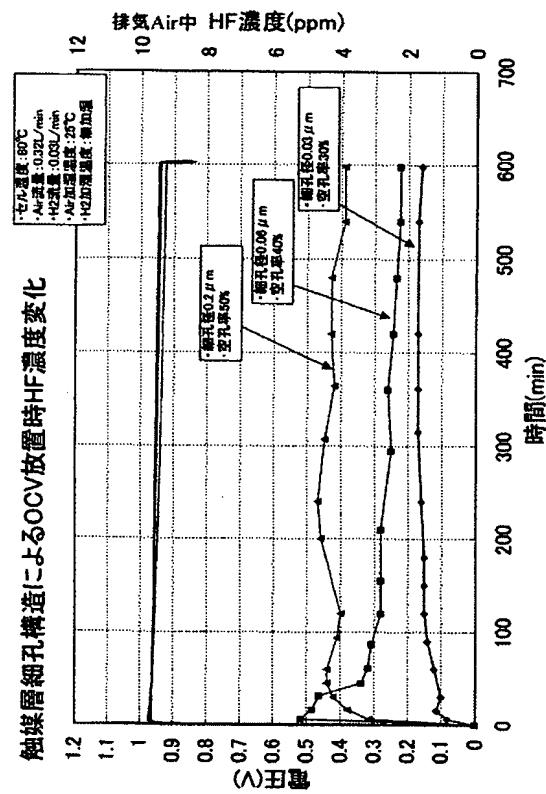
[Drawing 1]



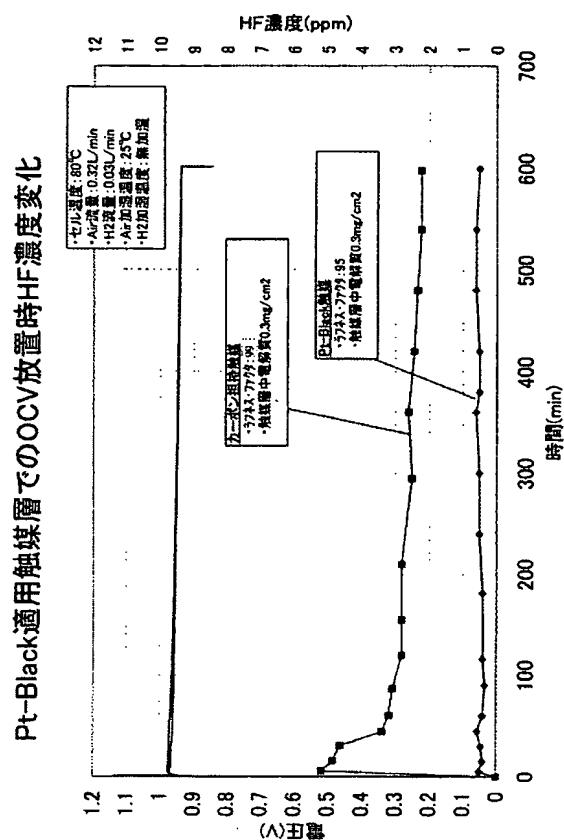
[Drawing 2]



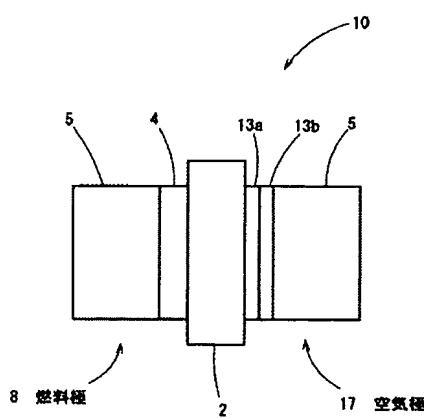
[Drawing 3]



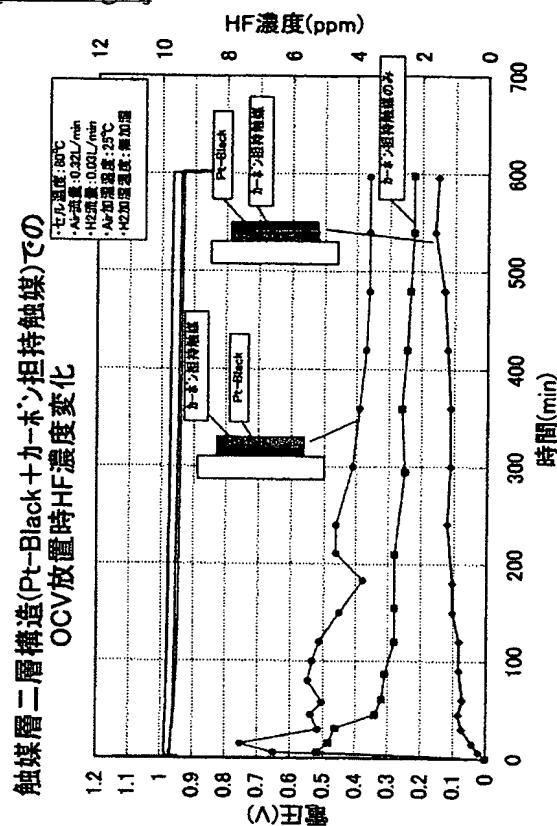
[Drawing 4]



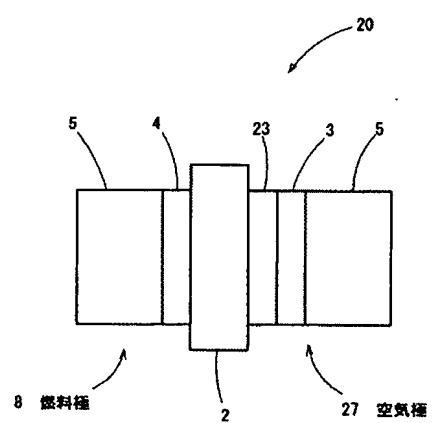
[Drawing 5]



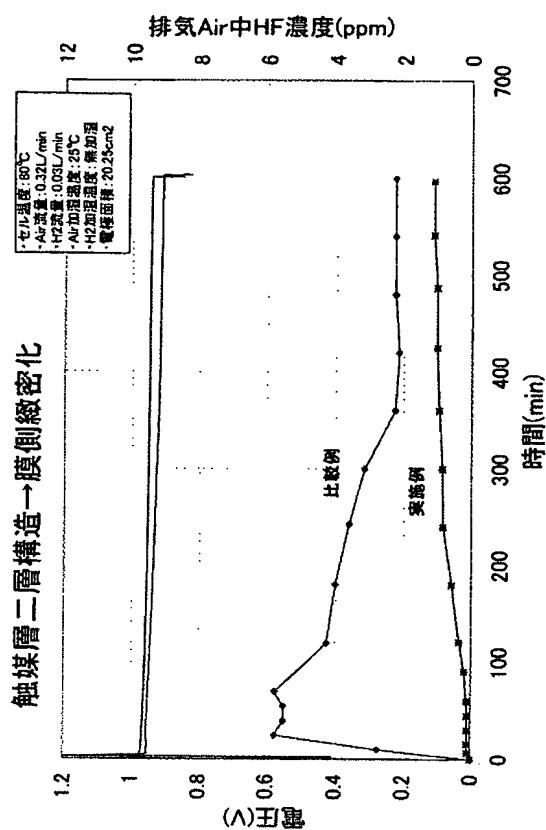
[Drawing 6]



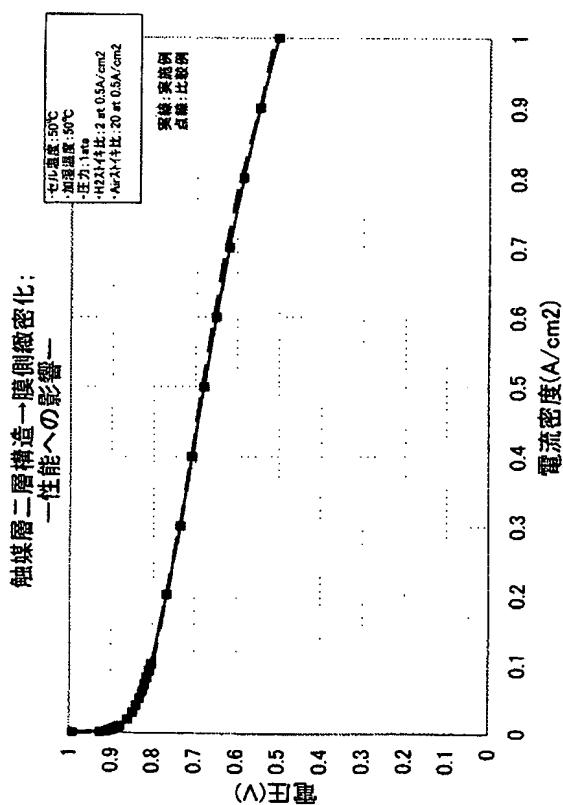
[Drawing 7]



[Drawing 8]



[Drawing 9]



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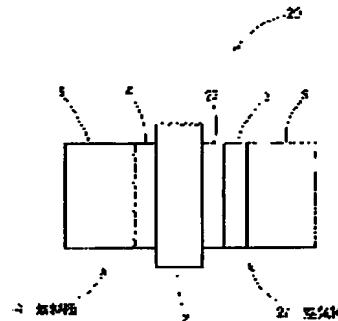
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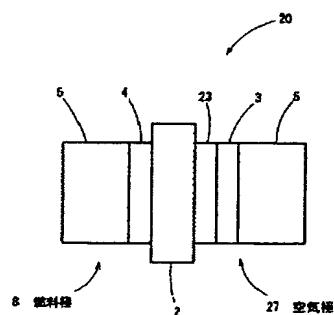
(54) 【発明の名称】燃料電池用電極

(57) 【要約】

【目的】燃料電池の空気極側触媒層において、電解質膜を透過した水素に起因するラジカルで電解質高分子材料が分解されることを防止する新規な方法を提案する。

【構成】空気極側触媒層を電解質膜側の第1の触媒層と拡散層側の第2の触媒層とから構成し、第1の触媒層の気体移動抵抗を第2の触媒層のそれよりも高くする。

【選択図】図7



【特許請求の範囲】

【請求項 1】

燃料電池に用いられる電極であって、その空気極側は電解質膜に触媒層及び拡散層を積層してなり、前記触媒層は前記電解質膜側の第1の触媒層と前記拡散層側の第2の触媒層とを備え、前記第1の触媒層は前記第2の触媒層よりも気体移動抵抗が大きい、ことを特徴とする燃料電池用電極。

【請求項 2】

前記第1の触媒層の細孔径は前記第2の触媒層の細孔率より小さい、ことを特徴とする請求項1に記載の燃料電池用電極。 10

【請求項 3】

前記第1の触媒層の空孔率は前記第2の触媒層の空孔率より小さい、ことを特徴とする請求項1に記載の燃料電池用電極。

【請求項 4】

請求項1～3のいずれかに記載の燃料電池用電極を備えた燃料電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】

この発明は燃料電池用電極の改良に関する。

【0002】

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【従来の技術】

燃料電池は、燃料極（水素を燃料極とする場合は水素極ともいう）と空気極（酸素が反応ガスであるので酸素極ともいう。また酸化極ともいう）との間に高分子固体電解質膜が挟持された構成である。

このような構成の燃料電池の起電力は、燃料極側（アノード）に燃料ガスが供給され、空気極側に酸化ガスが供給された結果、電気化学反応の進行に伴い電子が発生し、この電子を外部回路に取り出すことにより、発生される。即ち、燃料極（アノード）にて得られる水素イオンがプロトン（H, 0⁺）の形態で、水分を含んだ電解質膜中を空気極（カソード）側に移動し、また燃料極（アノード）にて得られた電子が外部負荷を通じて空気極（カソード）側に移動して酸化ガス（空気を含む）中の酸素と反応して水を精製する、一連の電気化学反応による電気エネルギーを取り出すことができる。 30

【0003】

このような燃料電池において、空気極は電解質膜側から触媒層と拡散層を順次積層した構成である。この触媒層は、燃料電池により高い出力を得るために、ストラクチャーの発達したカーボンブラックを触媒担持に使用するなどして、空孔率を上げたり、細孔径を大きくすることに主眼をおいて構成されていた。これは、反応に必要な酸素が空気中には約20%しか含まれていないため、高い性能を得るために触媒層により高いガス拡散性が求められているためである。即ち、触媒層におけるガス移動抵抗をできるだけ小さくすることにより、触媒層の全域へ充分量の空気が供給されるようになる。

【0004】

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【発明が解決しようとする課題】

しかしながら、この触媒層における高いガス拡散性は次の課題を有している。

燃料電池が開回路（OCV）状態や低負荷運転状態のときは、燃料極側に供給されている水素が発電により全て使われず、徐々に電解質膜を透過して、空気極側に到達する（この現象は電解質膜が薄いときに特に顕著になる）。空気極側に到達した水素の一部は微量でもFe⁺⁺などの金属イオンがコンタミとして含まれていると、これが触媒となって酸素と反応し、過酸化水素を生成する。この過酸化水素が酸性雰囲気下でヒドロキシラジカル（·OH）を生成する。このラジカルは強力な酸化力を有するので触媒層に含まれる電解質高分子材料をも酸化分解してしまうおそれがある。

そのため、従来では、過酸化水素発生の触媒となる金属イオンをキレート剤で捕捉したり 50

、また酸化防止剤を配合することにより電解質高分子材料が分解されること防止している（特許文献1～5参照）。

【0005】

【特許文献1】

特開2003-86187号公報

【特許文献2】

特開2003-20308号公報

【特許文献3】

特開2002-343132号公報

【特許文献4】

特開2001-223015号公報

【特許文献5】

特開2001-118591号公報

【0006】

【発明が解決しようとする課題】

キレート剤や酸化防止剤を添加することにより、電解質膜の高分子材料の分解は抑制されることとなる。

しかし、燃料電池システム内にかかる薬剤を添加することはコストアップにつながるばかりでなく、薬剤自体の安定性も確認されていない。

そこでこの発明は、過酸化水素による電解質高分子材料の分解を予防する新規な方策の提供を目的とする。

【0007】

【課題を解決するための手段】

本発明者は、過酸化水素による電解質高分子材料の分解防止につき鋭意検討を重ねてきたところ、「ラジカルは触媒層において専ら拡散層側（電解質膜から離れた部分）において発生すること」、を見出し、本発明に想到した。

即ち、燃料電池に用いられる電極であって、その空気極側は電解質膜に触媒層及び拡散層を積層してなり、

前記触媒層は前記電解質膜側の第1の触媒層と前記拡散層側の第2の触媒層とを備え、前記第1の触媒層は前記第2の触媒層よりも気体移動抵抗が高い、ことを特徴とする燃料電池用電極。

【0008】

このように構成された燃料電池用電極によれば、電解質膜を透過してきた水素の移動が第1の触媒層で妨げられるとともに、当該第1の触媒層において酸化され、拡散層側の第2の触媒層に到達する量が減少する。ラジカルは、空気極側触媒層のうちの拡散層側でより発生しやすいことが判明しているので、上記構造により、空気極側触媒層全体としてのラジカルの発生を抑制することができる。

【0009】

【実施の形態】

この発明は、既述のように本発明者が見出した空気極側触媒層における下記の特性に基づいている。

ラジカルは触媒層において専ら拡散層側（電解質膜から離れた部分）において発生すること。

【0010】

かかる知見は以下に説明する実験により得られた。

まず、図1に示す比較例の燃料電池1を作製した。この燃料電池1はナフィオン（DuPont社製Nafion112：商標名）からなる固体高分子電解質膜2を空気極側触媒層3と燃料極側触媒層4とで挟み、さらに各触媒層3、4の外側に拡散層5が形成されている。なお、この燃料電池1は図示しないケーシングで囲われており、このケーシングには空気極7へ空気を送排気するための孔と、燃料極8へ水素ガスを送排気するための孔

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が設けられている。

【0011】

空気極側触媒層3及び拡散層5は次のようにして形成された。

先ず、拡散層5を形成する。カーボンクロス（例えば日本カーボン社製G F - 2 0 - P 7（商品名））の両面に、撥水性カーボンブラック（例えば電気化学工業製デンカブラック（商品名））とP T F Eディスパージョン（例えばダイキン工業社製ポリフロンD - 1（商品名））を混合したスラリーを塗布し、窒素気流中360℃にて焼成する。このとき、塗布層のP T F E含有量は20～50%、塗布量は片面2～10mg/cm²とすることが適当である。

【0012】

続いて、P t 4 0 ~ 6 0 w t %の含有率のP t 担持カーボン粉末触媒と、電解質溶液（A l d r i c h社製5% N a f i o n（商標名）溶液）とを混合し、スプレー法若しくはスクリーン印刷法等により拡散層上に塗布・乾燥して空気極側触媒層3を得る。触媒持存量は触媒層面積当たり0.2～0.6mg/cm²とすることが好ましい。

空気極側触媒層3と拡散層5から空気極7が構成される。

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【0013】

他方、燃料極側触媒層4は次のようにして形成した。P t 2 0 ~ 4 0 w t %の含有率のP t 担持カーボン粉末触媒と、電解質溶液（A l d r i c h社製5% N a f i o n（商標名）溶液）とを混合し、スプレー法若しくはスクリーン印刷法等により拡散層上に塗布・乾燥して燃料極側触媒層4を得る。触媒持存量は触媒層面積当たり0.1～0.3mg/cm²とすることが好ましい。

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燃料極側触媒層4と拡散層5とで燃料極8が構成される。

【0014】

上記のようにして得られた空気極7と燃料極8の間に固体高分子電解質膜2を挟んで、ホットプレス法により接合する。ホットプレスの条件は温度：120～160℃、圧力：30～100kg/cm²、プレス時間：1～5分とすることが好ましい。

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【0015】

このようにして得られた図1の燃料電池1に事前に充分に通電処理を行って活性化した後、セル温度を80℃に設定し、両極7、8にドライN₂ガスを過剰量送って充分に乾燥させ、燃料電池1の状態を初期化する。これは、電解質膜2の初期の湿潤状態の違いによって、電解質膜の水素の透過量が変動するのを防ぐためである。この後、重水素（80℃、飽和加湿）を0.03L/分（ストイキ比4 at 0.05A/cm²）を燃料極8側に供給し、空気（室温、無加湿）を0.32L/分（ストイキ比17 at 0.05A/cm²）を送って燃料電池1を開回路状態で運転する。空気極7へガラス製のキャピラリの一端を接触させ、キャピラリの他端は高真空排気装置及び質量分析計へ接続する。キャピラリを介してサンプリングされた空気極7近傍のガス成分が質量分析計によりi n-situに同定される。

【0016】

図2に同定の結果を示す。図2において、最初の10分は初期化段階を示し、測定開始10分後に、重水素（D₂）ガスを燃料極8側へ供給した。その結果、過酸化重水素（D₂O₂）とフッ化重水素（D F）の濃度が増大している。これは、電解質膜2を通過した重水素が空気極側触媒層3において酸化されて過酸化重水素となり、この過酸化重水素が酸性雰囲気下においてラジカル（· D H）を生じ、これが触媒層3の電解質高分子材料を分解してフッ化重水素を生成したものと考えられる。

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【0017】

次に、図1の燃料電池において、空気極側触媒層3の細孔構造を変化させたときのフッ化水素（H F）の生成量をモニタした。結果を図3に示す。図中の下側のラインがH F濃度を示す。図3から空孔率が大きくなるにつれてH Fの濃度が高くなることがわかる。即ち、触媒層3が疎になりその気体移動抵抗が低くなるにつれヒドロキシラジカルの発生量が増大する。

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これは、気体移動抵抗が低い触媒層では、電解質膜2を通過してきた水素が容易に触媒層全体に行き渡るため、ラジカル生成源である過酸化水素が発生しやすくなるためと考えられる。

図3の結果より、「触媒層が疎（気体移動抵抗小）なほど過酸化水素の発生量が増え、他方触媒層が密（気体移動抵抗大）なほどその発生量が減少すること、」が確認できる。なお、図3の測定条件は図中記載の通りである。各サンプルにおける出力電圧はいずれも1V弱である。

【0018】

図1の燃料電池1において、空気極側触媒層4としてPt担持カーボン触媒が用いられていたが、これをPt-B1ackとしたもの（他の製造条件は同じ）についての開回路状態でのフッ化水素発生の状態を図4に示す。触媒層4においてPt担持カーボン触媒を有するものとPt-B1ack触媒を有するものとのラフネスファクタを統一し、両者の気体移動抵抗を実質的に等しくした。

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図4の結果から、Pt-B1ack触媒を採用した場合にフッ化水素の発生量が顕著に減少していることがわかる。これは、白金上に吸着された酸素分子が容易に解離するため、電解質膜2を透過してきた水素と反応して水が生成するだけで、ラジカル生成源である過酸化水素が生成し難いためではないかと考えられる。

【0019】

既述のようにPt担持カーボン触媒に比べてPt-B1ack触媒ではフッ化水素の発生量が小さくなることを前提として、図5に示すように、空気極側触媒層を2層構造（第1の触媒層13a、第2の触媒層13b）として、いずれか一方をPt担持カーボン触媒からなる層とし他方をPt-B1ack触媒からなる層とした。なお、図5において図1と同一の要素には同一の符号を付してその説明を省略する。このような空気極側触媒層を有する燃料電池10を開回路動作させたときのフッ化水素生成量をモニタしその結果を図6に示す。

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図6の結果から、Pt-B1ack触媒層を拡散層5側に配置したとき、フッ化水素の生成量が顕著に低下していることがわかる。Pt-B1ack触媒層はHFの発生が小さいことに鑑みれば、ラジカルの発生箇所は触媒層において拡散層側に位置することが推定される。

図4及び図6の結果から、本発明者による今回の新たな知見、「ラジカルは触媒層において専ら拡散層側（電解質膜から離れた部分）において発生すること。」が確認できる。なお、図6の測定条件は図中記載の通りである。各サンプルにおける出力電圧はいずれも1V弱である。

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【0020】

図7に実施例の燃料電池20を示す。図7において図1と同一の要素には同一の符号を付してその説明を省略する。

実施例の燃料電池20では、拡散層5へ空気極側触媒層（第2の触媒層）3を図1の場合と同様にして形成する（膜厚：約10μm）。その後、Pt担持カーボン粉末触媒と電解質とを混合し乾燥させた粉体の細孔分布を測定することにより、第2の触媒層3より空孔率及び／又は細孔径が小さく気体移動抵抗が大きくなるものを事前に選定する。この触媒と電解質溶液を混合し、スプレー法、スクリーン印刷法などにより第2の触媒層3の上にこれを塗布・乾燥して第1の触媒層23を形成し（膜厚：約2～5μm）、実施例の空気極27とする。この第1の触媒層23は第2の触媒層3よりもその組織が緻密であり、気体移動抵抗が高い。実施例において、この第1の触媒層23における触媒担持量は触媒層の面積当たり0.01～0.2mg/cm²とした。

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【0021】

このようにして得られた実施例の燃料電池20を開回路動作させたときのフッ化水素発生量をモニタしその結果を図8に示す。比較例は図1の燃料電池1のフッ素発生量を示す。なお、図8の測定条件は図中に記載の通りである。各サンプルにおける出力電圧はいずれも1V弱である。

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図8の結果から、実施例の燃料電池20によれば、試験開始10時間(600分)後の平衡時においてもフッ化水素の発生量が比較例の約1/2に低減していることがわかる。これは、電解質膜2を透過してきた水素の移動が密な構成の第1の触媒層で妨げられるので、ラジカルを発生しやすいポテンシャルを有する第2の触媒層まで達する水素の絶対量が小さくなり、もってラジカル発生源となる過酸化水素の発生量が触媒層全体として小さくなつたためと考えられる。

【0022】

空気極側触媒層に気体移動抵抗の高い第1の層を設けると、空気の拡散性が低下して燃料電池の出力特性が低下することが危惧される。しかしながら、図9に示すように、実施例の燃料電池(図7)は比較例の燃料電池(図1)と実質的に同等の電圧電流特性を示した

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。つまり実施例の燃料電池20によれば、動作特性を維持した状態でラジカルの生成を抑制することができる。よって、電解質高分子材料の分解が抑制され、安定した発電能力が維持されることとなる。

【0023】

図7の例では空気極側触媒層を2層構造としているが、これを3層構造ないしそれ以上の多層構造とすることができる。この場合、各層の気体移動抵抗を電解質膜側から拡散層に向けて順次小さくしていくことが好ましい。更には、空気極側触媒層において電解質膜側から拡散層にむけてその気体移動抵抗を漸減していくこともできる。

【0024】

本発明者により、空気極側触媒層では拡散層側の部位においてより多くのラジカルの発生することが確認された。したがって、当該部位へ集中的にラジカル発生防止手段を施すことにより、空気極側触媒層の特性低下を効果的に図ることができる。当該ラジカル発生防止手段としては、緻密層の使用(図3参照)、Pt-B1ack触媒の使用(図4参照)の他、特許文献1~5で提案されているキレート剤や酸化防止剤の使用が考えられる。

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【0025】

【発明の効果】

以上説明したように、請求項1の発明によれば、空気極側触媒層として電解質膜側の第1の触媒層と拡散層側の第2の触媒層とを備え、第1の触媒層の気体移動抵抗を第2の触媒層より高くした。これにより、電解質膜を透過してきた水素の移動が第1の触媒層で妨げられるとともに、当該第1の触媒層において酸化され、拡散層側の第2の触媒層に到達する量が減少する。ラジカルは、空気極側触媒層のうちの拡散層側でより発生しやすいことが判明しているので、上記構造により、空気極側触媒層全体としてのラジカルの発生を抑制することができる。よって、空気極側触媒層における電解質高分子材料の分解が抑制され、その性能が安定維持される。

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請求項2の発明によれば、請求項1における気体移動抵抗を高めるために、第1の触媒層の細孔径は第2の触媒層の細孔径よりも小さくした。この構造により空気極側触媒層全体としてのラジカルの発生を抑制することができる。

請求項3の発明によれば、請求項1における気体移動抵抗を高めるために第1の触媒層の空孔率は第2の触媒層の空孔率より小さい。この構造により空気極側触媒層全体としてのラジカルの発生を抑制することができる。

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さらにこれらの燃料電池用電極を燃料電池に適用した請求項4の発明によれば、燃料電池の寿命が向上することとなる。

【0026】

この発明は、上記発明の実施の形態及び実施例の説明に何ら限定されるものではない。特許請求の範囲の記載を逸脱せず、当業者が容易に想到できる範囲で種々の変形態様もこの発明に含まれる。

【図面の簡単な説明】

【図1】図1はこの発明の比較例の燃料電池の構成を示す模式図である。

【図2】図2は比較例の燃料電池のD₂、O₂及びDFの発生を示すチャートである。

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【図3】図3は空気極側触媒層における気体移動抵抗の大きさとHFの発生（即ちラジカルの発生）の関係を示すチャートである。

【図4】図4は空気極側触媒層においてPt担持カーボン触媒とPt-Black触媒とHFの発生（即ちラジカルの発生）の関係を示すチャートである。

【図5】図5は実験例の燃料電池の構成を示す模式図である。

【図6】図6は図5の燃料電池におけるHFの発生（即ちラジカルの発生）の関係を示すチャートである。

【図7】図7は実施例の燃料電池の構成を示す模式図である。

【図8】図8は実施例及び比較例の燃料電池のHFの発生（即ちラジカルの発生）の関係を示すチャートである。

【図9】図9は実施例及び比較例の燃料電池の動作特性（電流電圧特性）を示すチャートである。

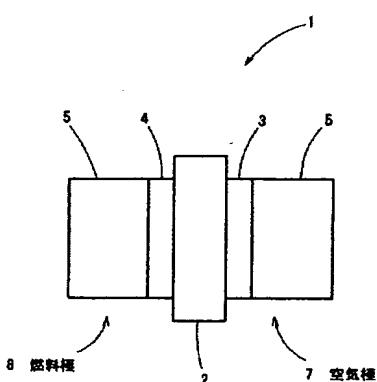
【符号の簡単な説明】

1、10、20 燃料電池
 2 電解質膜
 3 空気極側触媒層
 4 燃料極側触媒層
 5 拡散層
 7 空気極
 8 燃料極
 13a、23 第1の触媒層
 13b、3 第2の触媒層

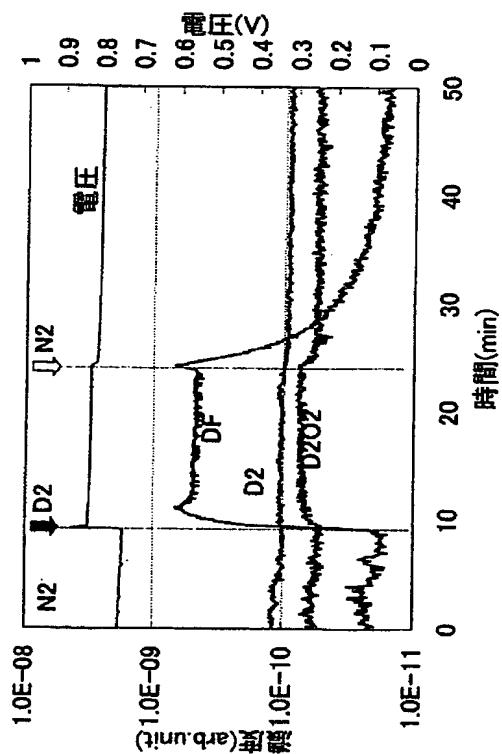
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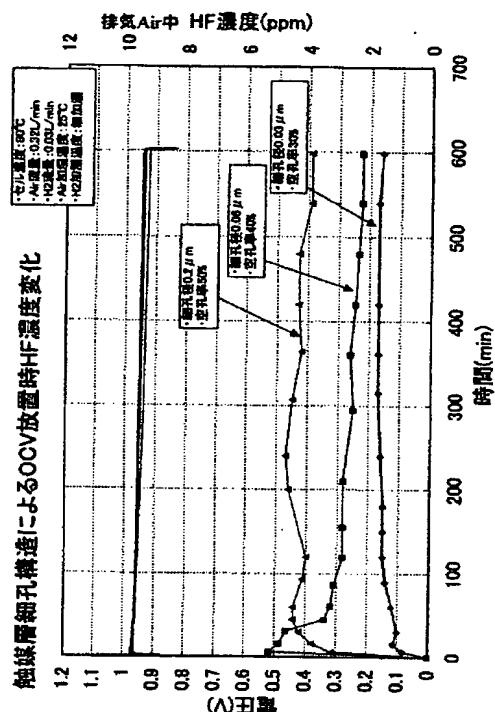
【図1】



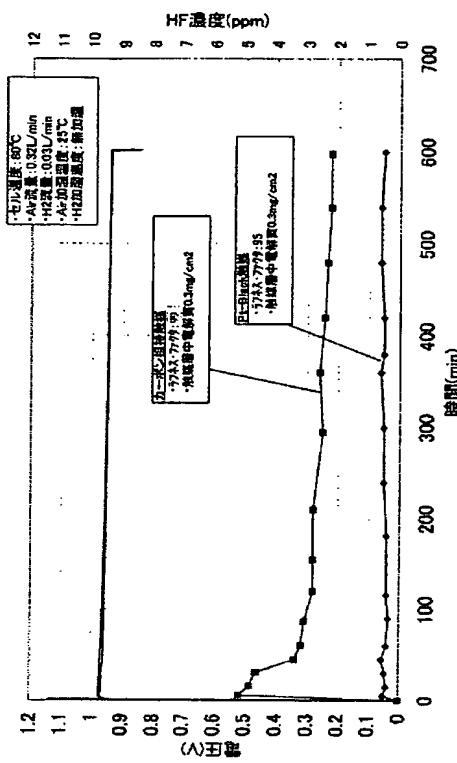
【図2】



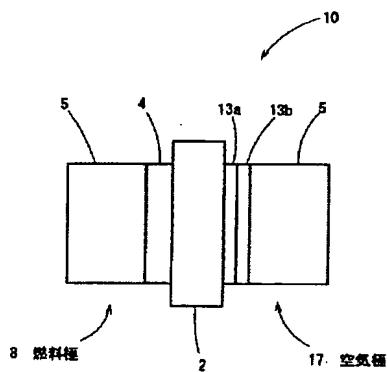
【図 3】



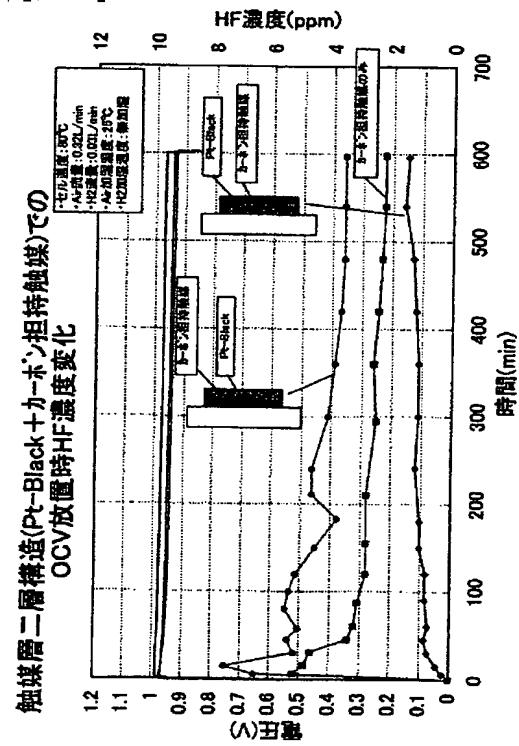
【図 4】



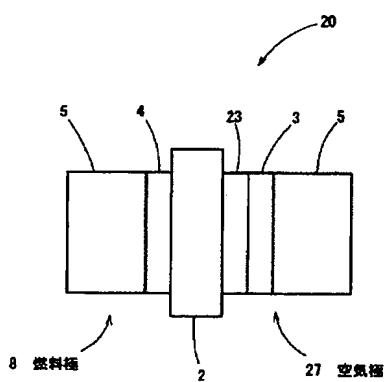
【図 5】



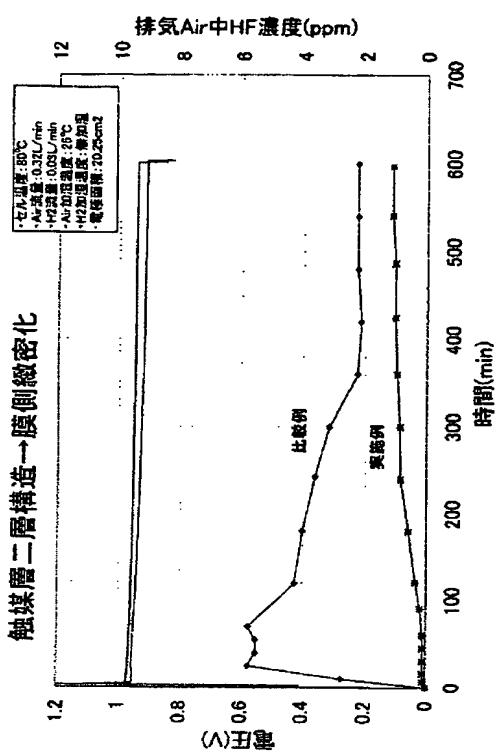
【図 6】



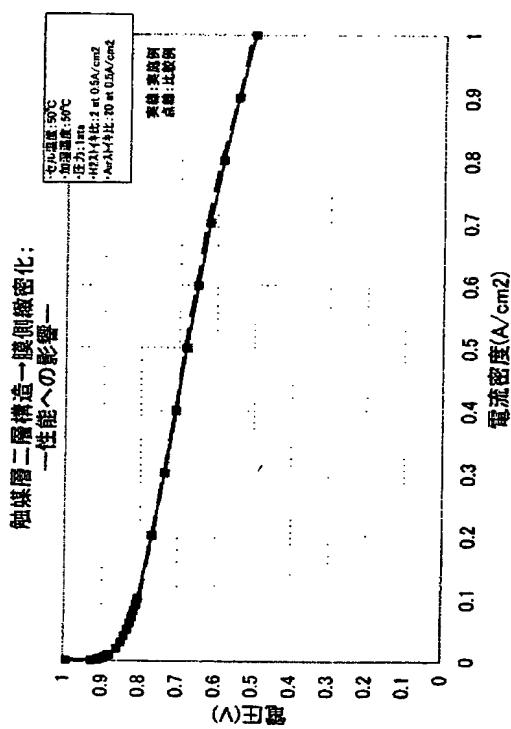
【図7】



【図8】



【図9】



フロントページの続き

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